IMPACT OF THE TREATMENT CONDITIONS OF A FORMIC/ACETIC ACID DELIGNIFICATION METHOD ON CHEMICAL STRUCTURE AND ANTIOXIDANT ACTIVITY OF BEECH WOOD LIGNIN

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CONTEXT AND OBJECTIVES

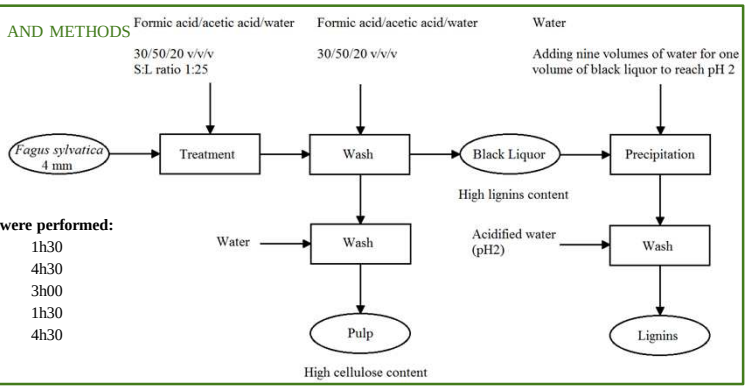
Lignin constitutes a promising resource for a sustainable production of organic compounds and biobased products that could progressively replace molecules from the petrochemical industry.

The study of lignin properties needs the development of extraction treatments and techniques of characterization.

In this study, a representative sample of beech wood (*Fagus sylvatica* L.) was collected in the region of Gaume in Belgium. Beech wood was delignified at atmospheric pressure by an organosolv process using a mixture of formic acid/acetic acid/water.

The effect of cooking time and temperature was evaluated on the structure, physico-chemical properties and antioxidant activity of the lignins obtained from the black liquor after treatments.

MATERIAL AND METHODS



5 treatments were performed:

1)	87°C	1h30
2)	87°C	4h30
3)	97°C	3h00
4)	107°C	1h30
5)	107°C	4h30

DELIGNIFICATION AND ANTIOXYDANT ACTIVITY

- ✓ Delignification ↗ with the cooking temperature and time
- ✓ Pulp yield ↙ when the cooking temperature and time ↗ (hydrolysis of hemicelluloses and cellulose)

Treatment	87°C 1h30	87°C 4h30	97°C 3h	107°C 1h30	107°C 4h30
Delignification yield (%)	8	16	28	42	**75**
Pulp yield (%)	89	84	77	68	55

- ✓ Antioxydant activity is assessed by a UV visible spectrophotometric method using the free radical DPPH [1]
  - Radical scavening index (RSI) is defined 1/EC50
  - EC50 (mg/ml) is the lignin concentration needed to decrease the initial DPPH concentration by 50%
  - RSI of lignins (97°C, 3h) = 13,66

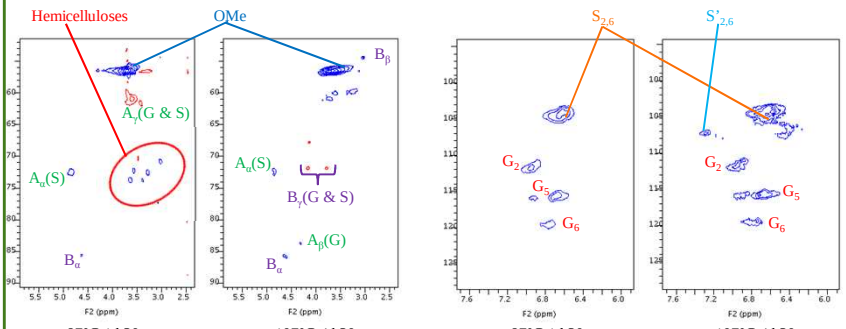
HSQC NMR ANALYSIS [2]

Side-chain region

→ gives information about the linkages between phenolic units

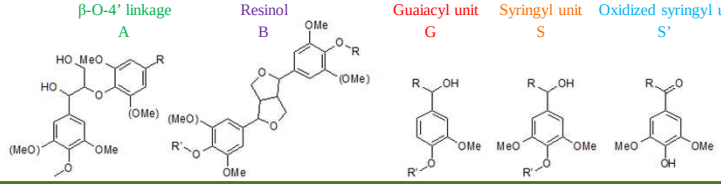
Aromatic region

→ gives information about the distribution of syringyl, guaiacyl and p-hydroxyphenyl units

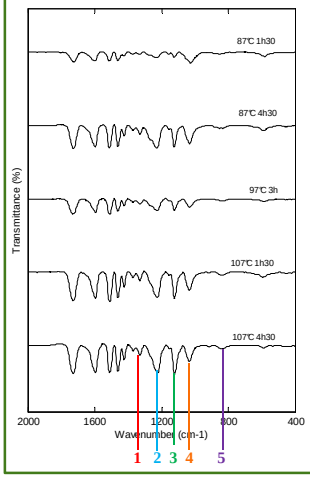


87°C 1 h30 | 107°C 4 h30 | 87°C 1 h30 | 107°C 4 h30

β-O-4' linkage A | Resinol B | Guaiacyl unit G | Syringyl unit S | Oxidized syringyl unit (Cα=O) S'

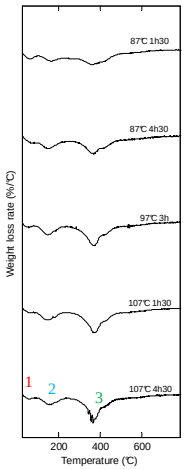


INFRARED ANALYSIS [3]



1) 1330 cm^{-1}: Syringyl units with C-O stretching
2) 1225 cm^{-1}: Syringyl and guaiacyl units with C-O stretching
3) 1124 cm^{-1}: Aromatic C-H in plane deformations (syringyl)
4) 1031 cm^{-1}: Aromatic C-H in plane deformations (syringyl and guaiacyl)
5) 833 cm^{-1}: Aromatic C-H out of plane deformations (syringyl and guaiacyl)

THERMOGRAVIMETRIC ANALYSIS [3]



Determination of the composition of lignin samples by the measurement of weight loss as a function of temperature

Different stages of decomposition are indentified:

1) Between 50 – 100°C: evaporation of water
2) Between 100 – 200°C: evaporation of acetic acid
3) Between 250 – 500°C: degradation of lignins (and hemicelluloses)
   - ➢ Shouldering of the two degradation peaks
   - ➢ Hemicelluloses degradation begins before lignin degradation

CONCLUSIONS

Delignification increases with the cooking temperature and time. Moreover, with high cooking temperatures and times, a repolymerisation of lignins occurs. Indeed, HSQC NMR results shows the apparition of oxidized syringyl units.

Lignin samples present an antioxidant activity due to the presence of free phenolic hydroxyl groups [2].

Finally, when the formic/acetic acid treatment is soft (1h30, 87°C), HSQC and TGA results indicate the presence of hemicelluloses associated with obtained lignins.

REFERENCES

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[3] Vanderghem C. *et al.*, 2011. *Ind. Crops Prod.*, Article in press.

* Mathilde Simon is financially supported by FRIA (Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture).